TI-25320 Patent Amendment

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Park, et al. Application No.: 09/173,129 Filed: 10/15/1998 Title: Selective Oxidation for Semiconductor Device Fabrication Attorney Docket No.: TI-25320	Group Art Unit: 2814 Examiner: Peralta, G. Tech Grp Fax: TC 2800 AF: 703-872-9319 I hereby certify that this correspondence is being ☐deposited with the United States Postal Service as first class mail with sufficient postage in an envelope addressed to Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, or ☒facsimile transmitted to the U.S. Patent and Trademark Office, on 10/23/2003 Name: [signature] Date: 10/23/2003

Mail Stop AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER RULE 131

Dear Sir:

I, Boyang Lin, hereby declare:

1. I am one of the named inventors in this patent application.

2. I am currently employed by Texas Instruments Incorporated at its Dallas, Texas location, and I have been employed by Texas Instruments Incorporated at its Dallas, Texas location since at least as early as March 2, 1998.

3. On information and belief, attached to this Declaration as Exhibit A is a true and correct copy of an electronic mail generated by Ming Hwang, a co-inventor in the present application and an employee of Texas Instruments Incorporated at the time the invention was made, to other employees of Texas Instruments Incorporated, including me. This electronic mail was generated at least as early as March 2, 1998, as indicated by the date at the top of the page.

4. Exhibit A describes the safe use of a N_2O and H_2 system for the oxidation of a portion of an insulating layer and a silicon-containing structure while leaving a conductive structure substantially unoxidized. Exhibit A includes a copy of a previous electronic mail from Ming Hwang with specific ideas for safely using N_2O and H_2.

5. Attached to this Declaration as Exhibit B is a true and correct copy of a page from my engineering notebook prepared in connection with my employment at Texas Instruments Incorporated at least as early as March 2, 1998, as indicated by the dates next to my signature at the bottom of each page. These pages were read and understood by at least one of my co-workers at least as early as March 2, 1998, as indicated by his dated signature.

6. Exhibit B describes an O_2 and H_2 system as a safer alternative to N2O and H_2; since the N_2O and H_2 system had been operated safely, an O_2 and H_2 system should be able to operate safely as well. Furthermore, since the N_2O/H_2 system had been shown to oxidize a portion of an insulating layer and a silicon-containing structure while leaving a conductive structure substantially unoxidized, it was hypothesized that an O_2 and H_2 could be used to do the same.

7. Exhibit C is an electronic mail sent by me to my own mailbox detailing a meeting between myself (and other Texas Instruments Incorporated employees) and employees of Applied Materials, Inc. (AMAT), the assignee of U.S. Pat. No. 6,037,273,

including Gary E. Miner, an inventor on U.S. Pat. No. 6,037,273. This electronic mail was sent at least as early as March 2, 1998 as indicated by the date at the top of the page.

8. Exhibit C states that Texas Instruments Incorporated (TI) initiated the issue of using a O_2/H_2 system. Under the direction of Texas Instruments Incorporated, AMAT was to perform safety calculations on various systems including O_2/H_2, N_2O/H_2, and CO_2/H_2 systems.

9. Exhibit D is an electronic mail sent by me to other TI employees and to Gary Miner and Joe Piccirillo of Applied Materials, Inc. This electronic mail was sent at least as early as March 2, 1998 as indicated by the date at the top of the page.

10. Exhibit D shows the N_2O/H_2 maximum safe operating pressure as calculated by Applied Materials (Section 1, entitled "N2O/H2 SAFETY CALCULATION IS DONE"). It also shows an initial calculation of the maximum safe operating pressure for an O_2/H_2 system (Section 2, entitled "O2/H2 SYSTEM CAN OPERATE AT A HIGHER PRESSURE") by Applied Materials. These calculations were made under the direction of Texas Instruments Incorporated (see Exhibit C).

11. Exhibit E is an electronic mail sent by me to other TI employees and to Gary Miner and Joe Piccirillo of Applied Materials, Inc. This electronic mail was sent at least as early as March 2, 1998, as indicated by the date at the top of the page.

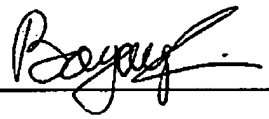
12. Exhibit E illustrates a final calculation by Applied Materials, Inc. (made under the direction of Texas Instruments Incorporated) of the maximum safe operating pressure at various levels of O_2 concentration in H_2. This calculation was performed under the direction of Texas Instruments Incorporated (see Exhibit C).

13. Exhibit F is an electronic mail sent by me to Gary Miner and Joe Piccirillo of Applied Materials, Inc. This electronic mail was sent at least as early as March 2, 1998, as indicated by the date at the top of the page.

14. Exhibit F includes a summary of the initial safety test for processing actual wafers in O_2/H_2 and N_2O/H_2 systems, confirming that processing performed within the calculated safe limits showed no indication of a destructive reaction. Further, the test shows actual resulting SiO_2 thicknesses for O_2/H_2 and N_2O/H_2 systems. These safety tests were performed under the direction of Texas Instruments Incorporated (see Exhibit C).

15. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Respectfully Submitted,



Boyang Lin

10/22/2003

Date

Exhibit A

Ming Hwang, 05:21 PM [redacted], N2O/H2 PROCESS (fwd)

Return-Path: <hwang>
From: hwang (Ming Hwang)
Subject: N2O/H2 PROCESS (fwd)
To: ashwin (Ashwin Shah), abernath (Joe Abernathy), bowling (Allen Bowling), scottk (Scott Kilpatrick), schichijo, wwsh@msg.ti.com
Date: Thu, [redacted] 17:21:10 -0600 (CST)
Cc: pas (Mike Pas), rmck@msg.ti.com, tiner (Paul Tiner), bolin (BoYang Lin), danderso (Dirk Anderson), hwang (Ming Hwang)
Content-Length: 3811

To: Ashwin Shah
Joe Abernathy
Allen Bowling
Shin Hasegawa
Scott Kilpatrick
Sam Shichijo

Copy: Mike Pas
Randy McKee
Paul Tiner
Bo-Yang Lin
Dirk Anderson

From: Ming Hwang

Subj: N2O/H2 PROCESS

Thank you very much for your help and support.

As Paul and Bo-Yang went UT Austin to evaluate selective oxidation process (N2O/H2 and other alternative chemistry) with Prof. Kwong this week, I would like to discuss with them to set up a schedule after they come back (Friday evening or next Monday).

I wish we could have a safe system/process to timely demonstrate selective smiling oxidation here at SPDC soon.

Thanks and Best Regards,

Ming Hwang

Forwarded message:
> From ashwin[redacted]
> From: ashwin (Ashwin Shah)
> Message-Id: <9612052059.AA09265@epcot.spdc.ti.com>
> Subject: N2O/H2 PROCESS
> To: hwang (Ming Hwang)
> Date: Thu, [redacted] 14:59:25 -0600 (CST)
> Cc: ashw%mimi@magic.itg.ti.com, abernath (Joe Abernathy), scottk (Scott Kilpatrick), bowling (Allen Bowling), shichijo (Sam Shichijo), wwsh%mimi@magic.itg.ti.com
> X-Mailer: ELM [version 2.4 PL23]

Printed for BoYang Lin <bolin@spdc.ti.com> 1

Exhibit A

Ming Hwang, 05:21 PM [redacted], N2O/H2 PROCESS (fwd)

> Mime-Version: 1.0
> Content-Type: text/plain; charset=US-ASCII
> Content-Transfer-Encoding: 7bit
> Content-Length: 2319
>
>
> To: Ming Hwang
>
> Copy: Joe Abernathy
> Allen Bowling
> Shin Hasegawa
> Scott Kilpatrick
> Sam Shichijo
>
> From: Ashwin Shah
>
> Subj: N2O/H2 PROCESS
>
> Ming,
>
> Thank you for your response. Please schedule a review with the copy to
> list above so that everyone is in agreement with this approach. Due to
> my schedule, I may not be able to attend, but I will depend on the
> recommendation from the team.
>
> Regards,
> Ashwin
>

> From: hwang (Ming Hwang)
> Subject: N2O/H2 process
> To: ashwin (Ashwin Shah)
> Date: Mon, [redacted] 10:55:11 -0600 (CST)
> Cc: bowling (Allen Bowling), abernath (Joe Abernathy), pas (Mike Pas),
> shichijo (Sam Shichijo), hasegawa, chapman (Dick Chapman),
> yang (Ping Yang), ih_chin (Ih-Chin Chen), danderso (Dirk
Anderson),
> richards (Bill Richardson), rmck@msg.ti.com, hwang (Ming Hwang)
>
> Ashwin,
>
> I am one of DRAM members who initiated a novel controllable selective
> oxidation technique using N2O/H2 system to solve metal oxidation problems
> during post-metal-gate-etch oxidation, MIM capacitor formation.
>
> We have demonstrated with Prof. Kwong of UT Austin that N2O/H2 system can
be
> operated safely because of:
>
> 1. a cold-wall single-wafer RTA system;

Exhibit A

Ming Hwang, 05:21 PM [redacted] N2O/H2 PROCESS (fwd)

> 2. N2O and H2 mixed ONLY in the chamber;
> 3. low pressure, low flow rate and low reaction volume;
> 4. N2O/H2 reaction ONLY localized (confined) to the heated wafer area;
> 5. no pressure surge during processing and N2O increase;
> 6. safety breaker installation with automatic H2 and power shutdown at pressure set point.
>
> The applications could be extented from post-metal-gate-etch oxidation and MIM
> capacitor formation to post poly-post-etch oxidation, high quality LPCVD SiO2
> deposition on metal wordline and bitline, high quality/low thermal budget NO
> dielectric formation and high quality ultrathin gate oxide formation.
> I think the above novel applications based on the simple and controllable
> N2O/H2 system can attract AMAT into a new business field.
>
> I am anxious to explain to you why we are so enthusiastic over this novel
> technique. I would be appreciated if you could set up a time for me to
> explain to you for this purpose.
>
> Thanks and Best Regards,
>
> Ming Hwang
>
>

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Exhibit B

[redacted]

Work of : Selective oxidation Date: 11/11/96

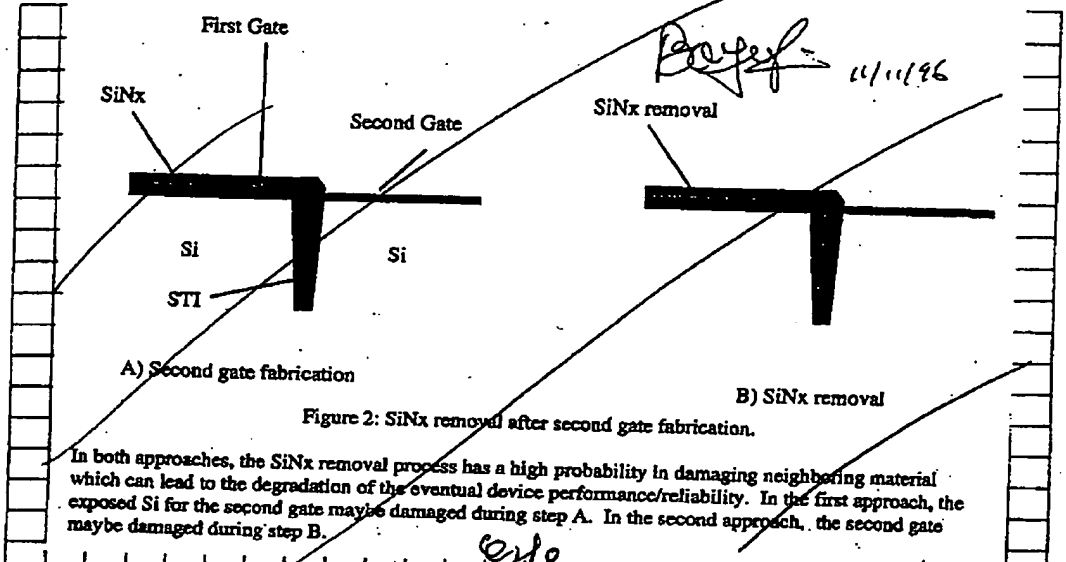

Figure 2: SiNx removal after second gate fabrication.

In both approaches, the SiNx removal process has a high probability in damaging neighboring material which can lead to the degradation of the eventual device performance/reliability. In the first approach, the exposed Si for the second gate maybe damaged during step A. In the second approach, the second gate maybe damaged during step B.

one

start here

Need to oxidize Si not W.

Existing: ① $H_2O + H_2$ H_2O is difficult to generate a flow

② $N_2O + H_2$ promising

$N_2O + H_2 \rightleftharpoons H_2O + 2NH_3 + 366KJ/mol$ ΔG

$O_2 + H_2$ is better

[redacted]

$\frac{1}{2}O_2 + H_2 \rightleftharpoons H_2O + 242KJ/mol$

O_2 flow easily controlled. less energy than N_2O.

[redacted]

[redacted]

Read and Understood By

Signed SHYH-HORNG YANG

[redacted] Date

Read and Understood By

Signed Date

Exhibit C

BoYang Lin, 02:53 PM [redacted] test

Return-Path: <bolin@spdc.ti.com>
Date: Fri, [redacted] 14:53:03 CST
X-Sender: bolin@epcot.spdc.ti.com
To: bolin@spdc.ti.com
From: BoYang Lin <bolin@spdc.ti.com>
Subject: test

Smiling Oxidation Program Update

When: [redacted]
Who: Bo Lin, Paul Tiner, Gary Miner
Format: conference call

1. Issues Discussed

A. Requirements
Oxidizing Si but not W.
Thermal budget is 900C, 8 mins for 55+-5A SiO2. Eventual requirement is 850C, 20 mins for 40+-5A SiO2.

B. Most Likely to Succeed Gary/Bo/Paul:
>From thermal budget requirement, H2O/H2 process is the most promising. At ATP, 50% H2O/H2, 900C, 1 minute, gives 60A of SiO2 (John Kuehne's data). With pure O2, 55A SiO2 requires 950C for 3 minutes.

C. Alternative Chemistry
TI raised the issue of using O2/H2 system. This is a dangerous system but so is N2O/H2. O2/H2 system is used in diamond growth (700-1000C) and at high temperatures the O2/H2 system may be equivalent to the H2O/H2 system. Since the H2O/H2 system will take a while [redacted] with possibility of being earlier), the O2/H2 system is worth investigating. An additional advantage of the O2/H2 system is that it is the best understood system.

D. Safety
AMAT will not use the mix-and-try approach to safety. AMAT will subcontract to experts to do the calculations. Also, AMAT would like to directly talk to UT on safety among other items with TI be the third party.

E. Wafers
AMAT would like to have 8" wafers and after a discussion, AMAT is willing to settle for 6" for initial evaluation.

Others
AMAT will be shut down until [redacted]

Action Items

WHAT	WHO	WHEN
TI contacts UT about 3-way conference call with AMAT		[redacted]

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Exhibit C

BoYang Lin, 02:53 PM [redacted], test

Bo [redacted]

Generating W/WN wafers for AMAT [redacted]
Bo

Equivalent thermal budget at different Temp to AMAT [redacted]
Paul/Bo

TI-AMAT-UT conference call [redacted]
All
(Reserved R&D conference room at 2 pm)

CO2 oxidation of Si wafers [redacted]
AMAT

W/WN wafers to AMAT [redacted]
Bo

AMAT safety calculation initial result (O2/H2, N2O/H2) [redacted]
AMAT

AMAT safety calculation completion (N2O/H2, O2/H2, CO2/H2) [redacted]
AMAT

More W/WN wafers to AMAT [redacted]
Bo

Identify safe parameter space (P, T, %) for W in N2O/H2 system [redacted]
AMAT

Within the safe space identified, what is the thickest SiO2 [redacted]
AMAT

Identify safe parameter space (P, T, %) for W in O2/H2 system [redacted]
AMAT

Within the safe space identified, what is the thickest SiO2 [redacted]
AMAT

IF CO2 system is feasible (identified by [redacted] do [redacted]
experiments on the CO2/H2 system.
AMAT

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Exhibit D

pas tiner hwang dan, 01:31 PM [redacted], Smiling Oxidation Update

To: pas tiner hwang danderso bolin mercer
From: BoYang Lin <bolin@spdc.ti.com>
Subject: Smiling Oxidation Update
Cc: gary_miner@AMAT.com Joe_Piccirillo@amat.com
Bcc:
X-Attachments:

[redacted]

1. N2O/H2 SAFETY CALCULATION IS DONE
(to be completed [redacted]; completed [redacted])

The maximum safe operating pressure is defined such that if detonation were to occur
instantaneously, the chamber pressure would not exceed 760 Torr (atm.). The safe pressure limit for different N2O concentration is shown below:

Concentration N2O in H2	Max. Operating Pressure
05 %	305 Torr
10 %	230 Torr
15 %	195 Torr
20 %	175 Torr
25 %	165 Torr

2. O2/H2 SYSTEM CAN OPERATE AT A HIGHER PRESSURE

Initial calculations show that at 20% O2 in H2, the pressure limit is 190 Torr, compared with 175 Torr for 20%N2O in H2. The equivalent O concentration for the O2 system is a factor of 2 higher than the N2O system.

3. EXPERIMENT TEMPERATURE

The temperature is chosen to be 950, 1000 and 1050C. We considered thermal budget and process time limit in determining the temperature range. At temperatures lower than 950C, the process time is too long and at temperatures greater than 1050C, the process time is too short to control.

4. ACTION ITEMS

Gary:

Task Present Date	Initial Date
1. Find out if W peels [redacted]	[redacted]
2. Finish O2/H2 safety calculation [redacted]	[redacted]
3. Experimentally determine safe N2O/O2 concentration [redacted]	N/A
4. Finish CO2/H2 safety calculation [redacted]	[redacted]

Exhibit D

pas tiner hwang dan, 01:31 PM [redacted] Smiling Oxidation Update

5. Determine SiO2 thickness at 950-1050C, %max and 2mins. NA

[redacted]

6. Start N2O/H2, O2/H2 experiment NA

[redacted]

7. Adapt system for 6" wafers NA

[redacted]

8. Finish "optimization" [redacted]

[redacted]

Initial Date is the initially agreed upon date. Present Date is now.

Exhibit E

pas tiner hwang dan, 04:19 PM [redacted], Smiling Update

To: pas tiner hwang danderso lu hsu bolin mercer gary_miner@AMAT.com
Joe_Piccirillo@amat.com
From: BoYang Lin <bolin@spdc.ti.com>
Subject: Smiling Update
Cc:
Bcc:
X-Attachments:

[redacted]

1. W IS PEELING (all)

Samples sent to AMAT for peeling tests indeed peeled. AMAT will send tested samples as well as remaining samples back to TI for analysis and modification. AMAT will not do any further testing eventhough the peeling is partial.

2. O2/H2 SAFETY CALCULATION IS DONE (Gary)
(to be completed [redacted]; completed [redacted])

The maximum safe operating pressure is defined such that if detonation were to occur
instantaneously, the chamber pressure would not exceed 760 Torr (atm.). The safe pressure limit for different N2O concentration is shown below:

Concentration O2 in H2	Max. Operating Pressure
05 %	273 Torr
10 %	220 Torr
15 %	201 Torr
20 %	193 Torr
25 %	189 Torr

The pressure limits are compable to the same % of N2O in H2. The O2/H2 system is advantageous because the equivalent O concentration for the O2 system is a factor of 2 higher than the N2O system.

3. SIMULATED TESTING (Mike Pas)

We will fabricate patterned poly-on-oxide and try oxidation under proposed conditions to see if indeed the expected thickening occurs.

4. ACTION ITEMS

Task	Who	Initial Date	Present Date
1. Find out if W peels	Gary	[redacted]	*[redacted]
2. Finish O2/H2 safety calculation	Gary	[redacted]	*[redacted]
3. Ship tested and remaining samples to Bo	Gary		*[redacted]
4. Ideas on improving adhesion	Bo(SPDC)		[redacted]
5. Experiments in improving adhesion	Bo(SPDC)		
6. Calculate P limit for 2% and 50% O2 in H2	Gary		

Printed for BoYang Lin <bolin@spdc.ti.com> 1

Exhibit E

pas tiner hwang dan, 04:19 PM [redacted], Smiling Update

7. Send new W wafers to AMAT Bo [redacted]
8. Peeling test Gary [redacted]
9. Experimentally determine safe N2O/O2 concentration Joe/Gary [redacted]
10. Determine SiO2 thickness at 950-1050C, %max and 2mins. Joe/Gary
2/7 [redacted]
11. Generate traveller for patterned poly Bo [redacted]
12. Finish CO2/H2 safety calculation Gary [redacted]
13. Adapt system to 6" wafers Gary NA
14. Finish "optimization" Joe/Bo [redacted]
15. Finish patterned wafers Bo
16. Program and safty review All
17.

Initial Date is the initially agreed upon date. Present Date is now.
* Task completed

Exhibit F

gary_miner@AMAT.com, 01:49 PM [redacted], Tasks and Updates

To: gary_miner@AMAT.com
From: BoYang Lin <bolin@spdc.ti.com>
Subject: Tasks and Updates
Cc: Joe_Piccirillo@amat.com, pas
Bcc:
X-Attachments:

Gary,

Couple things you need to do:

1: Please send me the peeling test results by the end of today.
2: Summary of the N2O/H2, O2/H2 results. A complete version will be very helpful.
3: When do you think the conversion to 6" will be done ([redacted]noon?). I need to make plane reservations.

Looking forward to getting your reply.

Thanks

Bo

Smiling Oxidation Program Update

When: [redacted]
Who: Bo Lin, Gary Miner, Joe Piccirillo
Format: conference call

A. Safety Experiment
AMAT has finished initial safty test. Safty tests close to the calculated limits show no indication of any destructive reaction indicating the calculation is fairly accurate.

B. Oxidation using O2/H2 and N2O/H2

The results are very encouraging, with 10% O2 in H2 at 190 Torr for a run time of 2 minutes, the silicon dioxide thickness is 31A/42A at 950C/1000C. At the same concentration of N2O or O2 in H2, the O2 system results in a thicker SiO2. The table shows the SiO2 thickness at 10% concentration, 950C and 190 Torr(?), for the O2 and the N2O systems:

O2	31A
N2O	22A

These results confirm TI's speculation.

C. N2O/H2 vs. O2/H2 system
The N2O/H2 system generates HNO3 and can be detrimental to long term system relibility. O2/H2 system is preferred from relibility point of view (AMAT).

Exhibit F

gary_miner@AMAT.com, 01:49 PM [redacted], Tasks and Updates

4. ACTION ITEMS

Task	Who	Initial Date
Present Date		
1. Find out if W peels [redacted]	Gary	[redacted]
2. Finish O2/H2 safety calculation [redacted]		Gary
3. Ship tested and remaining samples to Bo [redacted]		Gary
4. Ideas on improving adhesion [redacted]	Bo(SPDC)	
5. Experiments in improving adhesion [redacted]	Bo(SPDC)	
6. Calculate P limit for 2% and 50% O2 in H2 [redacted]	Gary	
7. Send new W wafers to AMAT [redacted]	Bo	
8. Peeling test [redacted]	Gary	[redacted]
9. Experimentally determine safe N2O/O2 concentration [redacted]	Joe/Gary	
10. Determine SiO2 thickness at 950-1050C, %max and 2mins. [redacted]	Joe/Gary	[redacted]
11. Generate traveller for patterned poly [redacted]		Bo
12. Finish CO2/H2 safety calculation [redacted]	Gary	[redacted]
13. Adapt system to 6" wafers [redacted]	Gary	NA
14. Finish "optimization" [redacted]		Joe/Bo
15. Finish patterned wafers [redacted]	Bo	
16. Program and safty review [redacted]	All	

* Task finished